

INTERIM SCIENTIFIC REPORT

Period: 1 March 1976 - 28 February 1977

HIGH RESOLUTION TRANSMISSION MEASUREMENTS

OF THE ATMOSPHERE IN THE INFRARED

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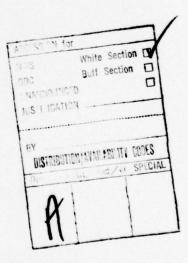
OF THE ATMOSPHERE IN THE INFRARED

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I. - INTRODUCTION

Thanks to the financial support of the belgian government, through the University of Liège, and to the Air Force Geophysics Laboratories Contract No. AFOSR-76-2985 through the European Office of Aerospace Research and Development (AFSC), the balloon program of the Institute of Astrophysics of the University of Liège was pursued in 1976; two flights were indeed carried out on April 22 and May 10, 1976, from the National Scientific Balloon Facility, Palestine, Texas.

The first flight (ULG-10) was devoted to near infrared solar observations, using lead sulphide detectors, both for single- and for double pass recordings. The following spectral intervals were recorded with a spectral resolution of about 0.035 cm⁻¹ in double pass and 0.08cm in single pass: 5757.1 - 5685.1 cm⁻¹; 5523.4 - 5465.1 cm⁻¹; 5438.0 - 5415.9 cm⁻¹; 5366.2 - 5227.3 cm⁻¹; 4879.1 - 4845.2 cm⁻¹; 4626.2 - 4607.04 cm⁻¹; 4061.6 - 4036.0 cm⁻¹.

Some of the above mentioned intervals were recorded at various solar elevations, in order to establish the effect of the air mass variation on some absorption lines suspected to be of telluric origin; this was particularly the case for the last mentioned interval which contains the R(1) line of the 1-0 band of hydrofluoric acid, located at 4038.97 cm⁻¹.

The equipment was launched at 06.40 Hr. A. M., local time, using a 87.7 \times 10³ cu. m. Winzen balloon which floated at an average altitude of 28 Km, until cut-down at 06.00 Hr. P. M.; the landing took place near Arcadia, Louisiana.

For the second flight (ULG-11), the spectrometer was equipped with a gallium-doped germanium bolometer and provided discrete solar observations, with 0.04 cm⁻¹ spectral resolution, in the following intervals: 3024 - 3007 cm⁻¹; 2937 - 2965 cm⁻¹; 1849 - 1830 cm⁻¹; 1620 - 1593 cm⁻¹; 1325 - 1259 cm⁻¹.

Here too, most of these intervals were scanned more than once.

The launch took place at 07.20 Hr. A. M., CDST; a Raven balloon, 122×10^3 cu.m., lifted the instrumentation to about 30 Km altitude; near noon, the gondola started a slow but regular descent, due to overheating of the balloon skin at the top-fitting seal. However, the cut-down command was not activated until 05.00 Hr. P. M., allowing some further observations to be made during part of the afternoon; observations had been planned until sunset.

An unpredicted "reversal wind", encountered by the descending parachute, brought the equipment down in Lake O' The Pine, Texas; recovery was not completed until 3 days later; the instrument was in very poor condition.

II. - SCIENTIFIC RESULTS

Until now, we have paid much attention to those spectral intervals into which telluric absorption features, of interest to the problem of pollution of the stratosphere, were present. This is particularly the case for the spectral region containing the R(1) line of the 1-0 band of HF, located at 4038.97 cm⁻¹.

It was indeed necessary, at the occasion of the 1976 flights, to check again for the presence of hydrofluoric acid in the upper stratosphere, as established in 1974 (Zander, 1975). The results of this investigation have been published in Geophysical Research Letters, under the title: "Confirming the presence of hydrofluoric acid in the upper stratosphere"; a copy of this paper is reproduced in Appendix A. It is worth, pointing out here, how useful the ground observations at the International Scientific Station of the Jungfraujoch have been in assessing the origin of the HF absorption feature at 4038, 97 cm⁻¹.

Based on our 1976 balloon and Jungfraujoch observations on HF, we have established a 3-steps profile represented on Figure 1 (no HF below 20 Km; 1.5 x 10⁻¹⁰ ppv between 20 and 28 Km; 3.6 x 10⁻¹⁰ ppv above 28 Km) this subjective distribution is larger, by about a factor 2, than theoretical predictions (Crutzen, 1975) but it represents the best trend deduceable from observations available till now; on Fig. 1, the curve labeled "Freons + Volcanos" is only indicative of the possible role which volcanos could play as sources of atmospheric HF (Cadle, 1975)

It should be mentioned here that more recently (March 1977), the R(1) line of HF was observed at the Jungfraujoch and that no Doppler shift (due to the variation of the earth-sun motion between autumn and spring) was observed for HF; this is a further argument corroborating the conclusion that the observed HF lines are of telluric origin.

A problem onto which we concentrate now, is the variability of atmospheric HF, both seasonal and within time intervals of about one week, as observed at the Jungfraujoch by Prof. L. Delbouille and Dr. G. Roland, on October 1976 and March 25 and 31, 1977. At first, we feel that these variations are indicative of short-time exchange processes between the stratosphere and the troposphere.

Figure 1

Also of interest for such processes, are the variations of the concentrations of both CH, and NO observed by balloon in the upper stratosphere: the same absorption lines observed at the same altitude, with the same spectral resolution, lead to average mixing ratios lower by at least 30% on May 1976, than for October 1974. The study of this type of seasonal variability is of major interest in the understanding of the long term stability of the stratosphere. Figure 2 shows, on a relative basis, our observed variation for N₂O; recent experimental results obtained by other investigations are also shown on that figure. The determination of absolute concentrations for the two last mentioned species is a matter of choosing the good line strengths and line half-widths among all those existing in the literature; recent laboratory efforts, carried out under very high spectral resolution conditions, are likely to settle such ambiguity (e.g. Toth et al., 1977, for CH₄). Aside of the investigations mentioned here before, we are currently analyzing data collected, both by balloon and at the Jungfraujoch, concerning telluric hydrochloric acid; conclusions on this subject are in progress and will be reported later.

We include, as Appendix B, a paper summarizing recent results about another objective of our balloon program, i. e. the observation and identification of photospheric lines in the middle infrared.

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Belgian support allows us to repair and still improve the instrumentation in terms of spectral quality; indium antimonide detectors, new gratings and transfer optics should allow to attain 0.02 cm⁻¹ resolution between 2.0 and 5.2 microns. Thanks to the continuation of the present AFOSR contract and to NASA's intervention in oversease expenses (which implies a collaboration with Professor L.D. KAPLAN of the Department of the Geophysical Sciences of the University of Chicago, Ill.), we hope to have another balloon campaign during the spring of 1978.

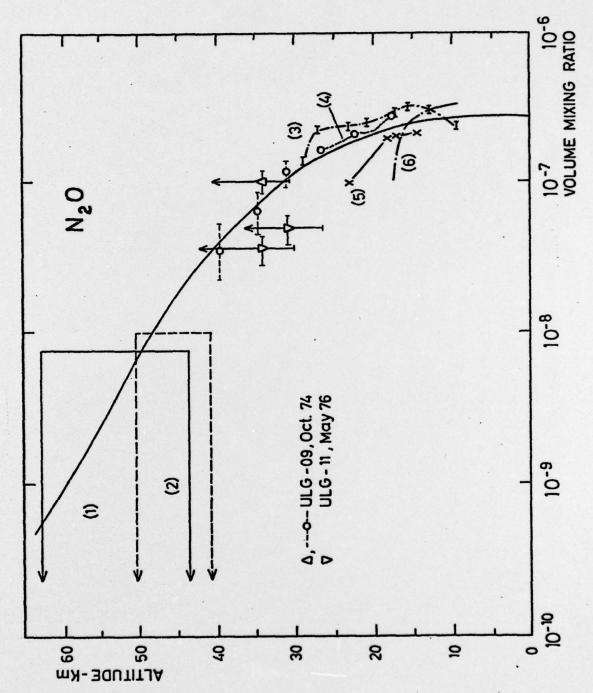


Figure 2

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CONFIRMING THE PRESENCE OF HYDROFLUOPIC ACID
IN THE UPPER STRATOSPHERE

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Abstract. Infrared solar observations made by balloon at 27.9 km altitude in April 1976, and from the ground station of the Jungfraujoch, Switzerland, in October 1976, have confirmed the presence of hydrofluoric acid in the upper stratosphere. An average value of (3.6 ± .7) x 10-10 ppv has been deduced for the concentration of HF above 27.9 km. The comparison between the groundand the balloon observations tends to indicate that over 50% of the total atmospheric HF is located above 25 km altitude.

Introduction

The diffusion into the stratosphere of a number of ground-released chlorofluorocarbons has been established experimentally [e.g., Murcray et al., 1975; Heidt et al., 1975; Schmeltekopf et al., 1975; Williams et al., 1976a]. Their subsequent photodissociation by UV radiation, mostly above 25 km altitude, has been the subject of a large number of theoretical investigations, all of them pointing out the preoccupying implications which increasing stratospheric amounts of chlorofluorocarbons could have in the future, due to an alteration of the natural ozone layer [e.g., Molina and Rowland, 1974; Cicerone et al., 1974; Crutzen, 1974; Stolarski and Cicerone, 1974; Wofsy et al., 1975].

Among the many chlorofluorocarbon-

Among the many chlorofluorocarbonrelated species predicted in the stratosphere, a few of them have already
been observed unambiguously; to our
knowledge, this is the case for HC1

[Farmer et al., 1976; Ackerman et al.,
1976; Williams et al., 1976b] and for
Clo [Anderson, private communication,
1976]. In 1975 [Zander, 1975], we reported the first result on the presence of
hydrofluoric acid above 27.5 km altitude.
In this note, we present further experimental evidences about this finding.

Hydrofluoric acid is an "end-product" issued from the breakdown by photolysis of chlorofluorocarbons, mainly CFCl₃ and CF₂Cl₂. While HCl is also a product of the chlorofluorocarbon photochemistry,

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its concentration in the stratosphere may be influenced by natural and anthropogenic CCl4 [Cicerone et al., 1975], by reactions with CH4, OH, HO2, H2, eventually, by direct injection of material into the stratosphere during intense volcanic activity [Cadle, 1975]; such injection could also influence the HF amount above 20 km altitude, but to a less important extent. It appears, therefore, that hydrofluoric acid is a constituent whose monitoring should provide valuable indications concerning the evolution of the freon activity in the stratosphere.

Measurements of atmospheric HF

The first evidence of the presence of hydrofluoric acid in the upper stratosphere was reported in 1975 [Zander, 1975], following the identification on balloon-recorded solar spectra taken in September 1974, of the R1 line of the 1-0 fundamental band of HF, located at 4038.97 cm-1.

On a more recent flight (April 1976), carried out from the National Scientific Balloon Facility, Palestine, Texas, the solar spectrum was again recorded at 27.9 km altitude and some 20 scans were taken over the spectral interval 4038-4040 cm⁻¹. Figure 1 shows one set of such scans. SP-2 and SP-4 are two spectra recorded in single pass, with a spectral resolution of 0.08 cm⁻¹, obtained simultaneously with the double-pass spectra DP-2 and SP-4, whose resolution is 0.03 cm-1; these four spectra were taken when the sun was at about 54 degrees elevation. The six lower spectra of Fig. 1 were recorded in double-pass with a 0.04 cm⁻¹ resolution, while the solar elevation varied between 19 and 12 degrees ; each individual scan took about 2 minutes recording time; elapsed time between successive scans shown here, was approximately 5 minutes. The lines noted by a dot are due to solar CO; the position of one H2O line is indicated by a cross, while the HF-R1 line is marked by an arrow (note the difference in dispersion between the four upper traces and the other ones; the wavenumbers scale applies to the upper traces ;

Zander et al.: Hydrofluoric Acid

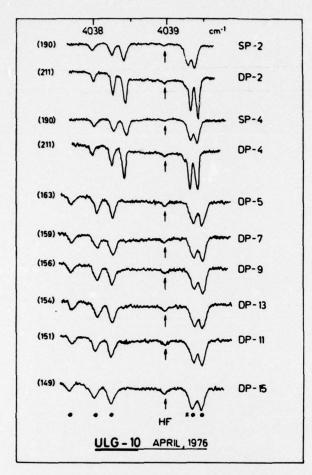


Fig.1. Solar spectra near 4039 cm⁻¹, taken from 27.9 km altitude, at various solar zenith angles (linear ordinate deflections).

numbers on the left of each trace indicate, in millimeters, the zero position

with respect to the continuum).

Even more recently (October 1976), we have observed the solar spectrum in the vicinity of 2.5 micrometers, from the International Scientific Station of the Jungfraujoch, located at 3580 m altitude in the Swiss Alps, using the very high spectral resolution instrumentation being currently operated there for solar observations [Delbouille et al., 1973].
Figure 2 shows two spectra obtained with a resolution of 0.02 cm⁻¹. Trace A is an average of 150 scans taken at solar zenith angles comprised between 56 and 60 degrees (individual scans were recorded at a speed of 0.7 cm^{-1} per second). A few solar lines due to carbon monoxide as well as absorption lines due to telluric water vapor (marked by small bars) are indicated on that trace. The absorption at 4038.97 cm^{-1} is at the position expected for the R1 line of HF. In order to ensure that this feature is indeed attributable to atmospheric HF, subsequent solar observations of the same spectral interval were made at a slightly

larger air mass (2.21) and through a somewhat wetter atmosphere above the station (atmospheric moisture was not monitored during the measurements presented here); traces of gaseous HF at ambient pressure and temperature were added in front of the entrance slit of the grating spectrometer. Trace B, which is an average of 40 scans, shows the spectrum obtained under these conditions. The absorption feature supposed to be due to HF increases in intensity; its halfwidth becomes significantly larger but it remains precisely centered on the line of trace A, observed at 4038.97 cm-1. This last result is a valuable piece of testing, reinforcing the conclusion that hydrofluoric acid is indeed responsible for the absorption observed on trace A at 4038.97 cm-1 and that it is located at a much lower pressure than that prevailing in the laboratory (490 mm Hg).

Discussion

Using a line strength for R1, S2250K = 74.2 cm⁻²Amagat⁻¹, deduced from value given by Connes et al. [1967], our 1976 balloon observations lead to an equivalent zenithal amount of HF above 27.9 km altitude, equal to 4.6×10^{-6} cm. Amagat; this corresponds to an average mixing ratio above that altitude, equal to $(3.6 \pm .7) \times 10^{-10}$ ppv. On the other hand, the Jungfraujoch equivalent zenithal amount of HF is 9.7 x 10cm.Amagat, about twice the balloon value. From these results, assuming HF to be equally distributed over Texas and Switzerland, we conclude that 50% of the total telluric HF lies above 27.9 km. With the line strength given previously, the average mixing ratio deduced from our 1974 balloon observations is equal to $(4.8 \pm 1.0) \times 10^{-10}$ ppv above 27.5 km ; the difference between the 1974 and the 1976 balloon results should be considered here as reflecting the observational uncertainties and difficulties; due to the much greater number of scans taken in 1976, we consider our last values much more reliable.

On a critical basis, we have further considered various possibilities likely to question (1) our identification as HF, (2) its being a telluric constituent, and (3) its location principally in the

upper stratosphere.

The increasing intensity of the 4038.97 cm⁻¹ absorption feature between high and moderately low sun observations at 27.9 km altitude (Fig. 1), indicates that the constituent responsible for that absorption is indeed in the earth's atmosphere. Furthermore, the half-width of that line as observed from the Jungfraujoch (Fig. 2, Trace A) is definitely narrower than the nearby lying solar lines of CO; if it had been formed by hydrogen fluoride present in the solar photosphere, its half-width should have

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Zander et al.: Hydrofluoric Acid

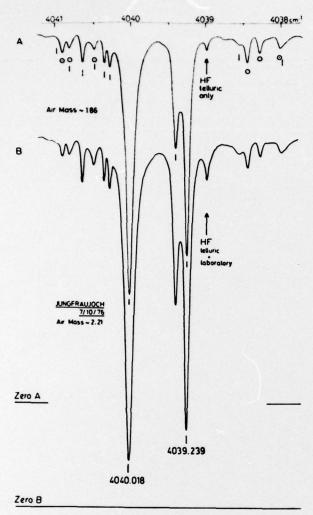


Fig. 2. Two solar spectra ranging from 4041 to 4038 cm⁻¹, as observed at the Jungfraujoch Station (linear ordinate deflections).

been wider than those of the CO lines (by a factor 1.4, equal to the ratio of the molecular weight of CO to that of HF). While it is not possible to exclude definitely a weak contribution due to traces of HF in the photosphere, theoretical calculations allow us to estimate that this contribution would amount to at most a 0.1 mA equivalent width for R1, which is less than 2% of the observed intensity [Hall and Noyes, 1969]. It is worth noting here that D.N. Hall [1970] has observed HF in sunspots, not in the photosphere. If any other telluric constituent (such as H₂O or CO₂) had been responsible for the observed line at 4038.97 cm⁻¹, it would have produced an absorption observed at the ground which would be much more intense than that observed at balloon altitudes. HF is the only stratospheric constituent likely to be responsible for the absorption feature discussed here. It should be mentioned that weaker lines (RO, P1,

P2) of the 1-0 fundamental band of HF also appear on the balloon spectra.

We would like to conclude this confirmation of HF by emphasizing the importance of the very high spectral resolution when trying to detect weak telluric absorption features due to constituents which may be present in the atmosphere at very low concentrations. Ground observations such as those reported here should be carried out on a regular basis for all constituents whose maximum concentration occurs in the stratosphere; when tied occasionally to higher-altitude observations (by aircraft or by balloons), they become even more useful and ultimately, they are likely to provide accurate temporal variations of the concentration of species produced in the stratosphere; this has already been verified for 03 and HNO3; it should be feasible as well for HF, HC1, C10, NO and NO2.

Acknowledgments. We thank Prof. G. Herzberg, Prof. M. Migeotte and Prof. D. Williams for having encouraged us to extend our 1974 observations on HF. Dr. E. Biémont made calculations about the contribution of photospheric hydrofluoric acid. Our balloon flights were made with the help of the National Center for Atmospheric Research, Palestine, Texas.

The balloon program was financially supported by the Belgian government and by the Air Force Cambridge Research Laboratories, Bedford, Mass., through the European Office of Aerospace Research, OAR, London, under the non-cost contract No AFOSR-72-2317.

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Research Note

Identifications of Solar Lines out to 8 µm, Based on Spectra Obtained by Balloon

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Received December 16, 1976

Summary. The identification of 32 atomic solar lines, obtained from high resolution infrared spectra $(3.3 < \lambda < 8.0 \,\mu\text{m})$ recorded during stratospheric balloon flights, is presented. For the first time, photospheric atomic lines have been identified with certainty out to $8 \,\mu\text{m}$.

Key words: atomic lines — solar spectra — infrared

1. Introduction

Many identifications of atomic lines in the near infrared solar spectrum have been previously published (Biémont and Grevesse, 1973a; Biémont, 1976). However, in the meantime, a new empirical model of the sun has been established (Vernazza et al., 1976) and new atomic and molecular data have appeared in the literature. Moreover, new high resolution photospheric spectra have been recorded recently, with a spectral resolution of about 0.04 cm⁻¹, using the stratospheric balloon equipment available at our Institute (Zander, 1976). The solar observations carried out at around 28–30 km altitude, cover some near- and intermediate infrared intervals, between 3.3 and 8 µm not accessible from the ground.

In this note, we present a summary of solar lines identified on these spectra which, to our knowledge, are the best ones presently available.

2. Instrumentation

The stratospheric equipment used to record the solar spectrum is basically composed of a 38.5 cm aperture telescope associated to a 2.5 m focal length Ebert-Fastie grating spectrometer used in double pass with a narrow intermediate slit. A description of the instrumentation and its spectral performances have been given elsewhere (Zander, 1970, 1972) and will not be repeated here. While lead sulfide detectors were selected for earlier observations between 1.7 and 2.9 μ m, more recent obser-

vations in the middle infrared range have been carried out, using gallium doped germanium bolometers cooled down to about 1.85 K by liquid helium (Zander, 1976).

Two flights (October, 1974 and May 1976) have already been devoted to solar observations above 3.0 μ m; for both practical and scientific reasons, only selected intervals were more specifically investigated during these flights. The spectral regions which have been used here are: 3.31–3.32, 5.40–5.49, 6.17–6.28, 6.44–6.56 and 7.66–7.99 μ m.

3. Results

The analysis of the solar spectra obtained in the mentioned spectral regions provides useful informations concerning some telluric constituents present in the upper stratosphere. Most of their absorption lines are rather easily detected on the basis of their half-widths, which, on our spectra, are narrower than those of the Fraunhofer lines; lines due to CH₄, N₂O, H₂O and CO₂ were identified by using the compilation of molecular parameters due to McClatchey et al. (1973). Wavelengths for CO were computed by Sauval (1976) using the fundamental data from Mantz and Maillard (1974), and kindly made available to us.

A number of Fraunhofer lines are also present on the spectra, even at the longest wavelengths. For these transitions, we have computed theoretical equivalent widths by using a method similar to that previously described (Biémont and Grevesse, 1973a) and we have compared the theoretical and experimental equivalent widths. The oscillator strengths used here are due to Biémont and Grevesse (1973b) (Coulomb approximation, $Z \le 20$) and to Kurucz and Peytremann (1975) (Scaled Thomas-Fermi-Dirac Method, $21 \le Z \le 28$) and the model considered is that of Vernazza et al. (1976). The following abundances have been adopted in agreement with the most recent compilations (Hauge, 1976; Withbroe, 1976; Ross and Aller, 1976); C: 8.55, Na: 6.25, Mg: 7.50, Al: 6.30, Si: 7.60, Fe: 7.50, in the usual scale where $\log N_{\rm H} = 12.00$.

Table 1. Identifications of atomic lines in the infrared solar spectrum (3.3 < λ < 8.0 μ m)

Element	λ ^C (μm)	λ ⁰ (μm)	WC(mA)	$W^0_\lambda(m\mathring{A})$	Identification
Cı	3.31241	3.3124	39.	60.	P(B:CH ₄)
Cı	3.31308	3.3131	19.	32.	P(B:CH ₄)
Cı	3.31454	3.3146	19.	24.	P(B:CH ₄)
Siı	{3.31588 3.31588	3.3159	163.	~ 190. }	P(B:CH ₄)
Cı	3.31670	_	51.		M(CH ₄)
Siı	3.317278	3.3173	250.	~ 202.	$P(B:CH_4+H_2O)$
Sit	3.31771	3.3179	35.	32.	P?(B:CH4+H2O)
Mgı	$ \left\{ \begin{array}{l} 3.319127 \\ 3.319169 \\ 3.319215 \end{array} \right\} $	3.3192	1031.	1410.	P(B:CH ₄ +?)
Alı	5.40586	5.4058	16.	20.	P
Alı	5.41302	5.4128	25.	~ 20.	P?
Fei	5.41981	_	14.		M(H,O)
Naı	5.4269	_	136.	-	M(H ₂ O)
Naı	5.4342	5.4343	78.	145.	P
Siı	5.43745	_	204	_	P?(B:CO+?)
Mgı	5.44260	5.4425	32.	24.	P
Siı	5.4506	_	27.	-	B(H ₂ O, CO)
Siı	5.45866	5.4586	368.	395.	P(B:CO)
Siı	5.46073	5.4607	309.	295.	P(B:CO)
Siı	5.4643	5.4643	65.	~ 60.	P(B?)
Fei	5.46905	5.4691	14.	26.	P
Mgı	${\left\{ \begin{matrix} 6.21992 \\ 6.22003 \\ 6.22012 \end{matrix} \right\}}$	6.2200	501.}	~ 410.}	<i>P</i> (<i>B</i> :H₂O)
Mgı	6.24110	6.2412	519.	576.	P
Alı	6.25859	6.2585	157.	110.	P
Alı	{6.27452 } 6.27454 }	6.2745	210.	216.	P
Fei	6.445663	6.4456	31.	49.	P
Siı	6.48185	6.4818	61.	64.	P(B:H2O)
Mg1 Si1	6.48417 }	6.4842	527. 51.	~ 706.}	P(B:H ₂ O)
Siı	6.49974	6.4996	51.	63.	P
Fei	7.6706	7.6710	24.	24.	P(B:CH4, N,O)
Siı	7.72154	_	34.	-	P(B:CH4, N2O)
Fei	7.8790	7.8791	22.	~ 32.	P
Siı	7.8968	7.8967	56.	56.	P(B: H ₂ O)

Note: In the column "Identifications", P is written for "Present", B, for "Blended", the molecules contributing to the blends being given between parentheses

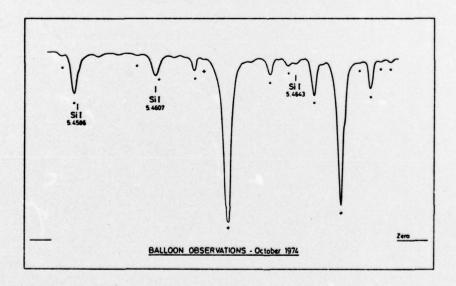


Fig. 1. Sample of the solar spectrum near $5.46~\mu m$ (see also the text)

The comparison between the experimental and theoretical data is summarized in Table 1, where we have successively indicated the element responsible for the absorption, the calculated wavelength in the air, $\lambda^{C}(\mu m)$, expressed in microns (obtained from the best available laboratory data), the observed wavelengths in the air, $\lambda^{0}(\mu m)$, also in μm , the calculated equivalent widths, $W_{\lambda}^{C}(m A)$, the measured equivalent widths, $W_{\lambda}^{O}(m A)$ (whenever this was possible) and finally the identification. Differences between the present and previously published equivalent widths are mainly due to changes in the model and in the abundances adopted.

Figure 1 represents a sample spectrum extending from 5.457 to $5.466 \, \mu m$, showing 3 atomic lines due to neutral silicon, solar CO lines indicated by dots and a few telluric lines noted by crosses. It must be emphasized that the measured wavelengths may be inaccurate because, in some cases, they were interpolated between nearby lying telluric lines whose wavelengths might be affected by large uncertainties.

4. Conclusions

In this short note, we have corroborated, with more accuracy, a few previous identifications of atomic lines above 5 μ m and we have extended such identifications out to 8 μ m. From now on, and contrarily to what was mentioned until recently (de Jager, 1975), one can state that solar lines have been identified with certainty above 5 μ m. Hopefully observations such as those which have

been used here, will be extended out to 13 µm at the occasion of forthcoming balloon flights.

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